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14. ABSTRACT The Navy wishes to develop predictive models describing transformations of CDOM, an assemblage of molecules defined as those that absorb ultraviolet and visible radiation. Our objective was to understand water-column biological processes hypothesized to affect both the "background" signature of CDOM as well as spatial and temporal changes in CDOM. We performed a series of laboratory experiments designed to understand CDOM transformations associated with micro- and macrozooplankton grazing on phytoplankton. Our approach was to use highly controlled laboratory experiments involving cultured representatives of grazers and prey, and to characterize the time course of CDOM transformations using spectroscopic and chemical techniques. There emerged no significant difference between experimental and control microcosms with respect to production and concentration of DOC and CDOM. Our series of experiments, therefore, stand in contrast to those reported by Strom et al. (1997), in which grazing by macro- and microzooplankton was shown to significantly increase DOC concentrations.

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FINAL REPORT

GRANT #: N00014-98-1-0639

PRINCIPAL INVESTIGATORS: Fred C. Dobbs and David J. Burdige

GRANT TITLE: Effects of Grazing by Macro- and Microzooplankton on Transformations of Colored Dissolved Organic Matter

AWARD PERIOD: 1 May 1998 - 20 June 2000

OBJECTIVE: To understand water-column biological processes hypothesized to affect both the "background" signature of colored dissolved organic matter (CDOM) as well as spatial and temporal changes in CDOM.

APPROACH: Our approach was to use highly controlled laboratory experiments, principally involving cultured representatives of grazers and prey (Dobbs) and to characterize the time course of CDOM transformations using spectroscopic and chemical techniques (Burdige). The two spectroscopic techniques were optical absorption (UV/Vis) spectroscopy and fluorescence excitation-emission matrix spectroscopy (EEMS). We coupled these spectroscopic measurements with molecular weight size fractionation studies to relate changes in CDOM optical properties with diagenetic transformations of DOM in general.

ACCOMPLISHMENTS: Over the course of this funding, we conducted a total of fifteen large-scale experiments, in addition to multiple "pilot" studies. Experiments #1-11 attempted to examine the production and character of CDOM associated with the effects of macrozooplankton grazing and initially employed as model systems the estuarine copepod *Acartia tonsa* and the phytoplankton *Skeletonema costatum* and *Isochrysis galbana*. In our attempts to reduce the high variance and seemingly unpredictable results characteristic of our early experiments, we subsequently switched to using only *Isochrysis galbana* as prey.

Experiments #12-15 were parallel efforts, but ones in which we attempted to ascertain the effects of grazing by microzooplankton on CDOM production. Our model systems in this case were the mixotrophic dinoflagellate *Oxyrhis marina* (the predator) and *Isochrysis galbana* (the prey).

In both sets of experiments, the essential design was to compare DOC and CDOM production between experimental microcosms (with grazers) and control microcosms (without grazers). We followed the dynamics of predators and prey in

the microcosms (1 to 2 liters) over time courses ranging from 72 to nearly 400 hours. There was, however, difficulty in obtaining consistent results between experiments. There seemed to be a higher degree of unpredictability than we ever anticipated.

We can make the overall statement that we generally saw an increase in total dissolved organic carbon with time, as well as an increase in humic-like fluorescence, which we use as an indicator of CDOM production. We found no evidence, however, that grazing was a significant input to the production of DOC and CDOM, even in experiments in which we actively attempted to discriminate between microbial decay of organic matter and that produced directly by grazing. That is, there was no consistent significant difference between experimental and control microcosms in either the rate of DOC production and its concentration or CDOM production and its characteristics.

We presented our in-progress results at ONR-sponsored CDOM workshops in 1999 and again in 2000.

<u>CONCLUSIONS</u>: Although both macro- and microzooplankton grazer experiments yielded insights into the ecology of predation, there emerged no significant difference between experimental and control microcosms with respect to production and concentration of DOC and CDOM. Our experiments, therefore, stand in contrast to those reported by Strom et al., in which grazing by macro- and microzooplankton was shown to significantly increase DOC concentrations. (Strom, S.L., R. Benner, S. Ziegler, and M.J. Dagg. 1997. Planktonic grazers are a potentially important source of marine dissolved organic carbon. Limnol. Oceanogr. 42: 1364-1374.)

<u>SIGNIFICANCE</u>: Studies of CDOM's properties, formation, and degradation are a current focus of ONR, given the Navy's present and projected needs for information about water visibility in the littoral zone. However, the contrast between our results and studies by Strom et al. (1997) suggest that renewed efforts (and possibly new approaches) will be required to further our understanding of grazing-related production of DOC and CDOM.

<u>PATENT INFORMATION</u>: No patents applied for.

AWARD INFORMATION: No awards.

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Burdige, D.J., S.W. Kline, L.S. Chasar, J.P. Chanton, P. Glaser and D.I. Siegel. 2000. Examination of dissolved organic matter (DOM) sources using fluorescence spectroscopy. EOS 80(49):OS21K-02. Presented at the 2000 AGU/ASLO Ocean Sciences Meeting. (A copy of the abstract is attached in the appendix.)

APPENDIX:

Burdige, D.J., S.W. Kline, L.S. Chasar, J.P. Chanton, P. Glaser and D.I. Siegel. 2000. Examination of dissolved organic matter (DOM) sources using fluorescence spectroscopy. EOS 80(49):OS21K-02. Presented at the 2000

Examination of Dissolved Organic Matter (DOM) Sources Using Fluorescence Spectroscopy

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Studies of DOM in natural waters using fluorescence excitation-emission matrix spectroscopy (EEMS) have observed different types of humic-like fluorescence, based on the unique excitation/emission wavelength maxima of peaks in these fluorescence spectra. Of the humic-like peaks observed to date (peaks A,C, and M), peak M is thought to have the strongest marinesource, while the other humic-like peaks have properties more similar to terrestrial humic substances. At the same time, however, it has also been suggested that diagenetic alteration of the fluorophore(s) responsible for peak M may lead to peak C fluorescence. To further understand the sources of refractory DOM in naturals waters using EEMS, we have examined sediment pore waters from estuarine (Chesapeake Bay), continental margin and shallow water carbonate sediments, and pore waters from a freshwater northern Minnesota peatland. Pore waters from Chesapeake Bay sediments suggest that there is a diagenetic relationship between the fluorophores responsible for peak M and C fluorescence, based on downcore variations in excitation and emission wavelengths of all humic-like peaks (i.e., peaks M, C, and A). In contrast, pore waters from shallow water carbonate sediments show both peaks M and C fluorescence in the same pore water samples, suggesting that distinct fluorophores are responsible for each of these types of fluorescence. Finally, pore waters from a freshwater northern Minnesota peatland show evidence of peak M and C fluorescence, with peak M fluorescence observed in fen samples and peak C fluorescence in closed bog samples. Possible explanations for all of these observations are that the fluorophores responsible for peaks M and C are always be present in natural waters, with the

relative concentrations of these fluorophores then affecting the occurrence of each type of fluorescence. For example, differences in organic matter sources and/or degradation pathways in different sedimentary environments may cause such real or apparent diagenetic changes in the composition of DOM humic-like fluorophores and thus explain these observations. These ideas will be explored in the context of previous suggestions discussed above regarding the sources of different types of humic-like fluorescence, and in terms of using EEMS to elucidate sources of refractory humic-like DOM.